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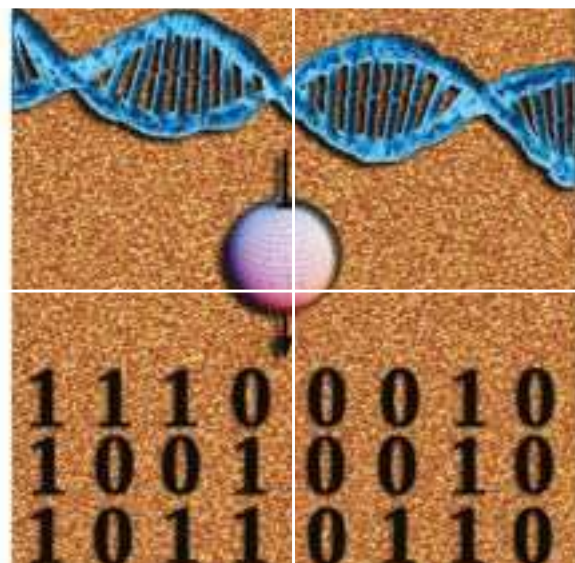
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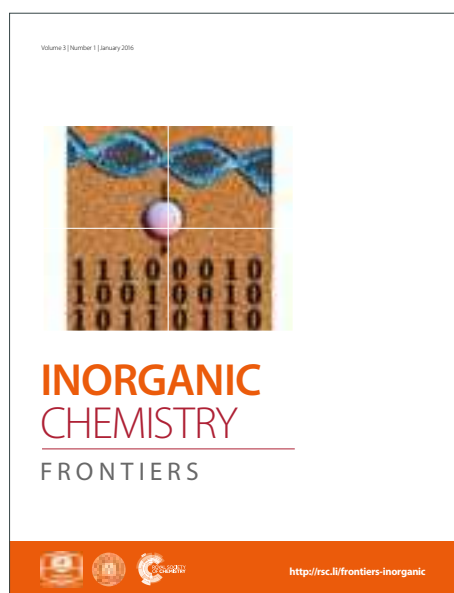
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Simple surface-assisted formation of palladium nanoparticles on polystyrene microspheres and their application in catalysis

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A facile and green approach has been developed for fabricating well-dispersed palladium nanoparticles (Pd NPs) supported on the surface of poly(*N*-vinylpyrrolidone) (PVP)-stabilized polystyrene (PS) microspheres. The strategy harnesses the reducing capability of PVP and the affinity between PVP and Pd NPs to achieve in situ surface-assisted growth of small noble metal NPs on the PS microspheres, without involving any additional stabilizer or reducing agent. The stabilizer-free formation contributes to the superior availability and accessibility of active sites for catalysis. The resultant PS/Pd composite particles have demonstrated excellent catalytic performance in the probe reaction of 4-nitrophenol reduction. As far as we know, this approach has been the first straightforward in situ deposition of Pd NPs on the PS microspheres, obviating surface treatment and the use of exogenous reducing agent or stabilizer. Furthermore, it is extendable to the fabrication of other composite systems, PS/Ag composite particles for example.

Introduction

To date, immense efforts have been devoted to the design and fabrication of nanostructured composite materials for potential applications in heterogeneous catalysis.^{1, 2} Among them, particular attention has been paid to the assembly of noble metal nanoparticles on the surface of inorganic or polymeric microspheres.³ The formation of this type of composite particles can effectively prevent the aggregation of small noble metal nanoparticles, which ensures the high availability and stability of active sites in the heterogeneous catalysis, thus contributing to excellent catalytic activity and reusability.

Therefore, lots of works have been done to develop the strategies for the flexible deposition of noble metal nanoparticles on various colloidal supports.⁴⁻¹¹ Conventionally, the noble metal precursors or reducing agents are at first attached onto the surface of support materials, followed by an in situ chemical reduction reaction.¹² Generally, in order to promote the deposition of noble metal nanoparticles, surface pretreatments of support materials with functional compounds are inevitable in most of the reported works, making the synthetic procedure tedious and time-consuming.

For example, polymer latexes and silica particles have been used as colloidal support after surface functionalizations or modifications with mercapto or amino groups, which can serve as anchor sites for the attachment of noble metal nanoparticles.¹³ In addition, the established approaches conventionally involve the use of organic solvents (e.g. DMF) and exogenous reducing agents (e.g. hydrazine and sodium/potassium borohydride) which may generate environmental hazard and biological toxicity.¹⁴ With the increasingly-growing concerns about economy, environment and sustainability, it is highly desirable to explore a straightforward and environmental-friendly synthetic approach for the immobilization of noble metal nanoparticles on the support materials.

In this paper, we report a facile and green approach to grow palladium nanoparticles (Pd NPs) in situ on the surface of polystyrene (PS) microspheres via a surface-assisted reduction. The common poly(*N*-vinylpyrrolidone) (PVP)-stabilized PS microspheres without any surface pretreatments were elegantly selected as colloidal support. The Pd NPs with controllable size can be readily obtained by in situ reduction of PdCl₂ by PVP in aqueous environment, omitting the use of harsh organic solvents, exogenous reducing agents and capping agents. The success of this strategy relies on the inherent reducing capability of PVP and the affinity between Pd NPs and PVP.¹⁵⁻¹⁷ The catalytic properties of the as-prepared PS/Pd composite particles were characterized by the standard reduction of 4-nitrophenol with NaBH₄. Lastly, the extendibility of this approach for fabricating other noble metal NPs supported on the PS microspheres was tested, by adopting [Ag(NH₃)₂]⁺ as one of the representative noble metal ions.

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Experimental

Materials

Styrene (St) and azodiisobutyronitrile (AIBN) were purchased from Sinopharm Chemical Reagent Co., and respectively distilled under vacuum and recrystallized before being used. Poly(vinylpyrrolidone) (PVP K-30), NaBH_4 , PdCl_2 , AgNO_3 , ammonia, isopropanol, HCl, and *p*-nitrophenol (4-NP) were obtained from Sinopharm Chemical Reagent Co. and used as received. Ultrapure water ($18.2 \text{ M}\Omega\cdot\text{cm}$) was used throughout the experiments.

Synthesis of Polystyrene (PS) Microspheres

The polystyrene microspheres were synthesized according to the method reported by Armes et al.¹⁸ PVP (3 g) dissolved in isopropanol (180 mL) was added to a four-necked round-bottom flask. The above solution was then heated to 70°C and simultaneously bubbled with nitrogen, eliminating any oxygen. AIBN (0.2 g) predissolved in St (20 g) was injected into the above reaction vessel under vigorous mechanical stirring and the polymerization was initiated. After 24 h of polymerization, the vessel was cooled to room temperature. The PS microspheres were collected by centrifugation and redispersed in water before use (solid content, 10 wt%).

Preparation of Polystyrene/Palladium (PS/Pd) and Polystyrene/Silver (PS/Ag) Composite Particles

The aqueous dispersion of PS microspheres (10 g, 10 wt%) was mixed with aqueous solution of PdCl_2 (3.33 mL, 0.03 M) in a round-bottom flask (50 mL). The mixture was heated and kept at 80°C for 5 h under shaking. Afterwards, the as-prepared PS/Pd composite particles were separated out by centrifugation/washing/redispersion cycles and finally dispersed in water. The synthetic process of PS/Ag composite particles is basically the same with PdCl_2 replaced with $[\text{Ag}(\text{NH}_3)_2]^+$.

Catalytic Reduction of 4-Nitrophenol (4-NP)

4-NP (30 μL , 0.01 M) aqueous solution, water (2.64 mL), aqueous dispersion of catalyst particles (30 μL), and freshly prepared NaBH_4 aqueous solution (300 μL , 0.1 M) were injected into a quartz cuvette. The kinetic process of the reduction reaction was monitored by the variation of absorbance at 400 nm as a function of time. To investigate the recyclability of PS/Pd composite particles, this reaction was amplified by ten times. After each run, the catalyst particles were recovered by centrifugation and reused directly for the next run. This procedure was repeated eight times.

Characterization

Transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDX) measurement were performed using a JEM-2100 microscope (JEOL Co., Japan). Scanning electron microscopy (SEM) measurements were carried out at an S-4800 instrument (Hitachi Co., Japan). X-ray diffraction (XRD) analyses were performed on a German Bruker-AXS D8 Advance. Inductively coupled plasma-optical emission

spectrometer (ICP-OES, Agilent, 700 Series) was used to analyze the Pd content in the composite particles. X-ray photoelectron spectroscopy (XPS) was recorded on a VG ESCALABMKII X-ray photoelectron spectrometer. UV-vis absorption spectra were collected on a SHIMADZU UV-3600 spectrometer at room temperature.

Results and discussion

In situ surface-assisted formation of Pd NPs on PVP-stabilized PS microspheres

Generally, PVP-stabilized PS microspheres were first prepared by a conventional dispersion polymerization method. PVP is a physiologically compatible and nontoxic polymer, and can be applied as either a reductant or a stabilizer to prepare the noble metal nanoparticles.^{16, 19} As shown in Fig. 1a, the as-prepared PVP-stabilized PS microspheres have uniform size (1.3 μm) and smooth surface. Afterwards, the preparation of PS microsphere supported Pd NPs (abbreviated as PS/Pd composite particles) was carried out by mixing selected volumes of aqueous dispersion of PS microspheres and PdCl_2 aqueous solution at 80°C . The reaction was allowed to proceed until the color of aqueous phase changed from pale yellow to dark grey.

In Fig. 1b, a representative SEM image of PS/Pd composite particles displays still good uniformity in morphology and size as compared with PS microspheres. More significantly, TEM observation (Fig. 1c) clearly displays that numerous dark spots distributed on the surface of PS microsphere. This phenomenon reveals the Pd NPs were successfully formed and deposited on the surface of PS microspheres. The average size of Pd NPs was determined to be ca. 4.5 nm, by examining randomly selected 200 Pd NPs in the TEM images, and the histogram of the size distribution has been shown in Fig. 1d. Moreover, ICP-OES analysis showed that the content of Pd NPs was about 0.92 wt% in the resultant composite particles. Notably, the size of Pd NPs on the PS microspheres can be

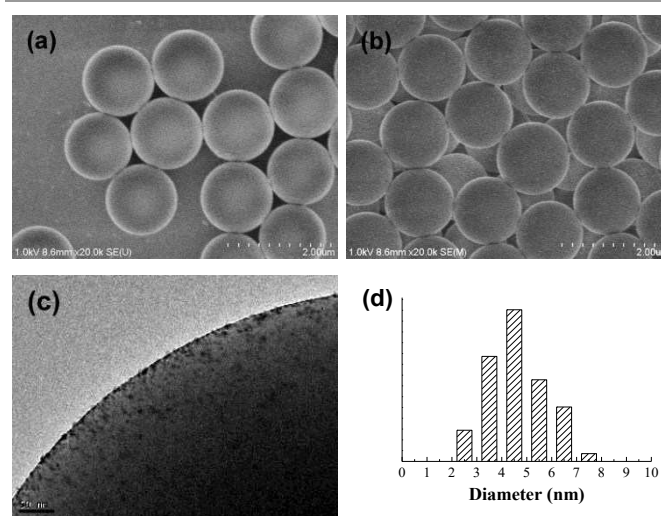


Fig. 1 SEM images of as-prepared PS microspheres (a) and PS/Pd composite particles prepared with the concentration of 33 mg/mL of PS microspheres (b); TEM image (c) and size distribution histogram of supported Pd NPs (d) of PS/Pd composite particles.

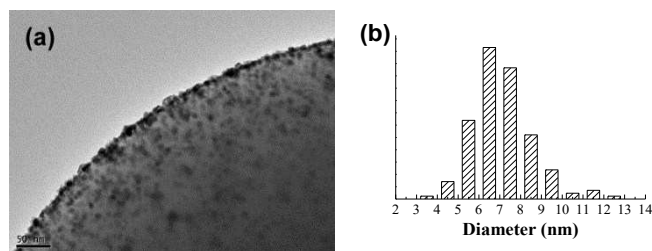


Fig. 2 TEM image (a) and size distribution histogram of supported Pd NPs (b) of PS/Pd composite particles prepared with the concentration of 3.3 mg/mL of PS microspheres.

easily controlled by changing the concentration of PS microspheres. As the concentration of PS was decreased from 33 mg/mL to 3.3 mg/mL, in Fig. 2, the immobilized Pd NPs became larger with an average size of about 7.0 nm, and the content of them was about 3.44 wt% in the resultant composite particles. In our approach, the PVP on the surface of PS microspheres served as reducing agent during the in situ formation of Pd NPs. The higher concentration of PS microspheres was expected to bring about increased amount of PVP, leading to the generation of more growth sites of Pd NPs, that is, smaller Pd NPs would be formed when the same amount of PdCl_2 was used.

The formation of Pd NPs on the surface of PS microspheres was further verified by the EDX spectroscopy, XPS, and XRD. In Fig. 3, the EDX spectrum clearly demonstrated the presence of Pd element in the as-prepared composite particles.²⁰ Fig. 4a

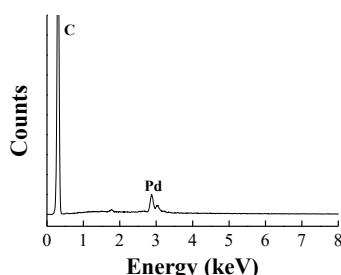


Fig. 3 EDX spectrum of PS/Pd composite particles prepared with the concentration of 33 mg/mL of PS microspheres.

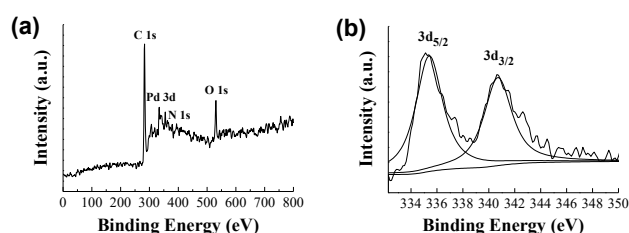


Fig. 4 XPS survey spectrum (a) of PS/Pd composite particles prepared with the concentration of 33 mg/mL of PS microspheres and core spectrum of Pd 3d (b).

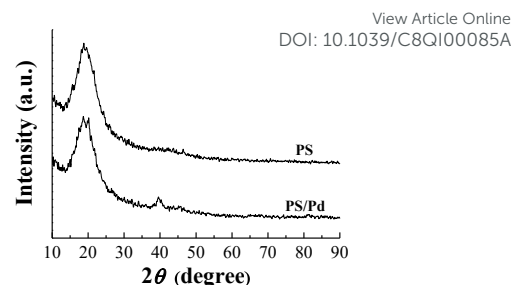


Fig. 5 XRD patterns of PS microspheres and PS/Pd composite particles prepared with the concentration of 33 mg/mL of PS microspheres.

depicts the XPS survey spectrum of PS/Pd composite particles. A strong doublet at around 338 eV can be discerned, which corresponds to photoelectrons originating from the Pd 3d energy level.²¹ Furthermore, the Pd 3d core spectrum in Fig. 4b displays the characteristic peaks of Pd 3d_{5/2} (335.4 eV) and Pd 3d_{3/2} (340.7 eV), consistent with the Pd⁰ state, corroborating the formation of Pd NPs on the surface of PS microspheres.²² The XRD patterns of the PS microspheres and PS/Pd composite particles are illustrated in Fig. 5. In comparison with the XRD pattern of PS microspheres, a new peak at around 39.8° corresponding to the (111) lattice plane of the Pd crystalline can be found in that of the PS/Pd composite particles.⁵ This broad and weak peak suggested that the Pd NPs were formed on the PS microspheres and their size was very small, which is in agreement with the TEM observations.²³ These results collectively demonstrate the successful formation of the PS/Pd composite particles.

Catalytic performances of PS/Pd composite particles

Motivated by the aforesaid structural features of the PS/Pd composite particles which favor the catalytic performance, such as well-dispersed ultrafine Pd NPs, large size of support microspheres and so on, we investigated the catalytic properties of our PS/Pd composite particles. We chose the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) by NaBH_4 in water as a model reaction, which has been used as a benchmark reaction to evaluate the catalytic activity of noble metal NPs supported on various substrates.²⁴ In general, without catalyst particles, this reduction reaction did not occur even with a large excess of NaBH_4 (Fig. S1, ESI†). Following the addition of trace amount of our PS/Pd composite particles (Pd NPs, *ca.* 4.5 nm), the absorption of 4-NP around 400 nm decreased rapidly, and a new absorption at around 300 nm appeared, which is attributable to the formation of 4-AP. The complete reduction was accomplished in 5 min, as shown in Fig. 6a. The gas bubbles of H_2 produced by NaBH_4 decomposition may have interfered with absorbance measurements, leading to the absence of isosbestic point in Fig. 6a. The peak at about 400 nm dominated during most of the reaction time, we hence investigated the reaction kinetics by deriving the concentration of 4-NP ions from the absorbance at 400 nm.^{25–27} Since the concentration of NaBH_4 greatly exceeded that of 4-NP, pseudo-first-order kinetics was used to calculate the reaction rate constant (k_{app}). In Fig. 6b, a linear relationship between $\ln(C_t/C_0)$ and the reaction time was obtained,

which well matched the first-order reaction kinetics. Thus, the k_{app} can be directly obtained by calculating the slop of this line and was found to be $1.09 \times 10^{-2} \text{ s}^{-1}$, when the concentration of Pd NPs (C_{Pd}) in the catalytic system was $8 \times 10^{-3} \text{ mM}$. We further measured the k_{app} in the same reaction systems at different C_{Pd} (4×10^{-3} and $2 \times 10^{-3} \text{ mM}$, Fig. S2, ESI[†]), finding that the value is proportional to C_{Pd} , as illustrated in Fig. 6d. Notably, similar phenomenon was also found when the PS/Pd composite particles (Pd NPs, *ca.* 7 nm) were used as catalyst particles (Fig. 6c, 6d and Fig. S3, ESI[†]). Therefore, from $k' = k_{app}/C_{Pd}$, we derived k_1 , which represents the intrinsic catalytic activity and allows a reasonable comparison with the results reported by other groups using supported Pd NPs.²⁸⁻³¹ The k' value was determined to be 1.42 and $0.90 \text{ s}^{-1} \cdot \text{mmol}^{-1} \cdot \text{L}$ for PS/Pd (Pd NPs, *ca.* 4.5 nm) and PS/Pd (Pd NPs, *ca.* 7.0 nm) composite particles, respectively.

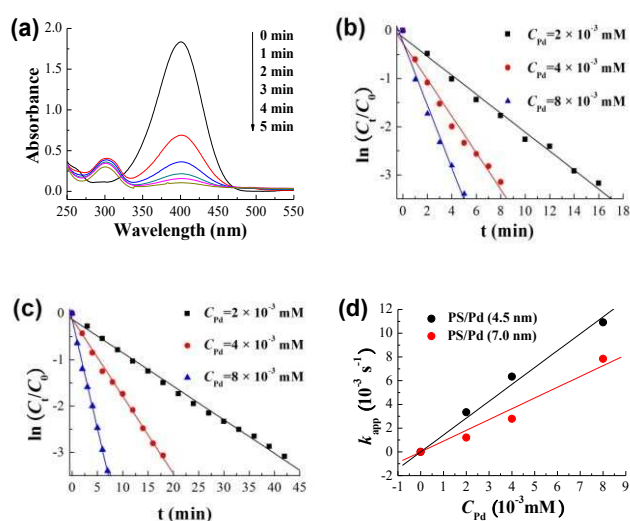


Fig. 6 UV-vis spectra of the reduction of 4-NP by NaBH_4 at different time with PS/Pd composite particles (Pd NPs, *ca.* 4.5 nm; $C_{Pd} = 8 \times 10^{-3} \text{ mM}$) as catalyst (a); plot of $\ln(C_t/C_0)$ versus time for the reduction of 4-NP by NaBH_4 catalyzed by PS/Pd composite particles of different C_{Pd} : Pd NPs, *ca.* 4.5 nm (b) and Pd NPs, *ca.* 7.0 nm (c); plots of the k_{app} as a function of C_{Pd} for different PS/Pd composite particles (d).

In Table 1, it is worth noting that the k' value for our PS/Pd composite particles with supported Pd NPs of *ca.* 4.5 nm is higher than most of previously reported k' values for the Pd NPs immobilized on different supports. Especially, similar catalytic study using preformed trisodium citrate-stabilized Pd NPs with smaller size (*ca.* 3.9 nm) immobilized on the PS microspheres exhibited a lower k' value than that of PS microsphere supported Pd NPs in this work. The excellent catalytic activity of our particles can be ascribed to the superior availability and accessibility of the active sites in the heterogeneous catalysis, which may result from (1) small size and high dispersity of Pd NPs on the PS microspheres; (2) existence of some ligand-free regions on the surface of Pd NPs,

Table 1 Summary of k_{app} , d_{Pd} , C_{Pd} , and k' for the reduction of 4-NP by different Pd NPs based catalysts. DOI: 10.1039/C8QI00085A

Catalyst	d_{Pd} (nm)	C_{Pd} (mM)	k_{app} (s^{-1})	k' ($\text{s}^{-1} \cdot \text{mM}$)	Ref
Pd/SBA-15	8.0	6.29×10^{-2}	1.18×10^{-2}	0.19	32
$\text{Fe}_3\text{O}_4/\text{Pd}@m\text{SiO}_2$	15.6	7.14×10^{-3}	1.60×10^{-3}	0.22	33
Pd-PEDOT-PSS	1-9	2.52×10^{-1}	6.58×10^{-2}	0.26	34
PPy/ TiO_2 /Pd	2.0	2.83×10^{-2}	1.22×10^{-2}	0.43	35
Pd-FG hybrid	15-20	4.72×10^{-3}	2.35×10^{-3}	0.50	36
K-TEA/Pd	4.5	1.77×10^{-2}	1.23×10^{-2}	0.70	37
PS/Pd ^a	3.9	8.00×10^{-3}	7.20×10^{-3}	0.90	38
p(MVCA-co-St)/Pd	5.0	1.98×10^{-3}	2.90×10^{-3}	1.47	11
$\text{Fe}_3\text{O}_4@ \text{CeO}_2/\text{Pd}$	3.0	7.47×10^{-3}	2.15×10^{-2}	2.88	39
PS/Pd	4.5	8.00×10^{-3}	1.09×10^{-2}	1.42	ours
PS/Pd	7.0	8.00×10^{-3}	7.84×10^{-3}	0.90	ours

^a Pd NPs were preformed and stabilized by trisodium citrate.

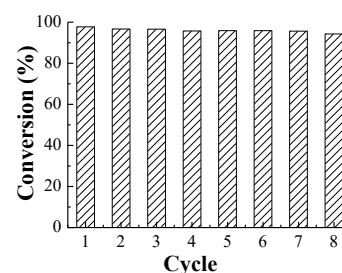


Fig. 7 The reusability of the PS/Pd composite particles (Pd NPs, *ca.* 4.5 nm; $C_{Pd} = 8 \times 10^{-3} \text{ mM}$) during eight cycles of the reduction of 4-NP by NaBH_4 .

which is the attributable to absence of any exogenous capping agents as stabilizers in the formation of Pd NPs.^{6, 40}

The reusability is also a crucial property for the practical applications of catalyst particles, and hence is further tested for our PS/Pd composite particles. The reduction reactions catalyzed by the same catalyst particles were performed for another 7 cycles. At the end of each cycle, owing to the large size of the PS microsphere, the PS/Pd composite particles can be readily recovered from the reaction solution by centrifugation and directly used in a next run. As shown in Fig. 7, after eight successive cycles of reduction reactions, the conversion remains higher than 95%. Significantly, these catalyst particles were reused without any surface treatment for activation, which is usually required to maintain the catalytic activity in the successive reactions in the majority of other reported catalysts. Therefore, taking practical applications into account, the PS/Pd composite particles reported here are promising to offer a type of reusable catalyst with high activity for liquid-phase catalytic reactions.

In situ surface-assisted formation of Ag NPs on the PVP-stabilized PS microspheres

In order to test the applicability of this strategy for preparing other composites of PS and noble metal NPs, $[\text{Ag}(\text{NH}_3)_2]^+$ is

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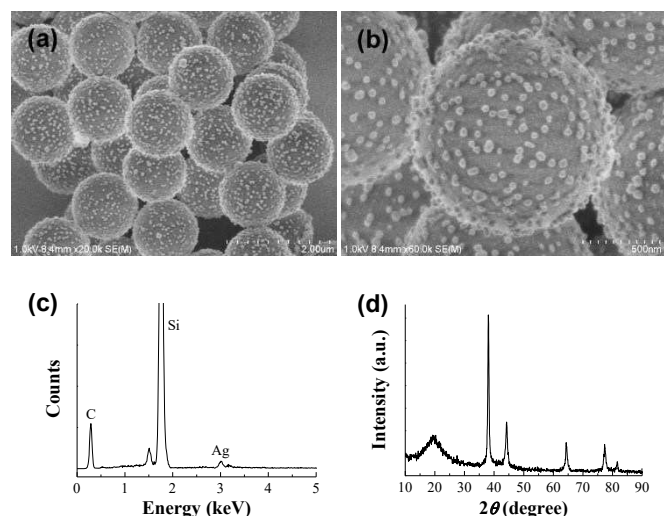


Fig. 8 SEM images of PS/Ag composite particles with low magnification (a) and high magnification (b). EDX spectrum (c) and XRD pattern (d) are shown.

selected as one of the typical noble metallic ions. As can be seen from Fig. 8a and 8b, the as-obtained sample shows a uniform distribution of Ag NPs with the size of ca. 45 nm on the PS microspheres. Furthermore, the formation of PS/Ag composite particles has been demonstrated by their EDX spectrum (Fig. 8c) and XRD pattern (Fig. 8d). These results suggest that this route is readily extendable to the deposition of other noble metal NPs on the PS microspheres.

Conclusions

In summary, the present work demonstrates that PS microsphere supported Pd NPs can be prepared via a simple and environmental-friendly approach based on the in situ surface-assisted reduction. Our approach avoids the tedious and time-consuming surface modification process, and the use of hazardous reducing agent, organic solvent or exogenous stabilizers in the formation of Pd NPs. The resultant PS/Pd composite particles possess high availability and accessibility of the active sites of the catalysts, and accordingly exhibit superior catalytic activity. They also show excellent recyclability, hence holding great potential for practical catalysis applications. In addition, our strategy is extendable to the fabrication of other supported metal nanoparticles (e.g. Ag NPs) for a wide region of potential applications.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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